LETTERS TO THE EDITOR

ON THE MEAN AMPLITUDE OF ATOMIC VIBRATION AND NATURE OF BONDING IN SOLIDS

The root-mean square amplitude \( \langle \dot{a}^2 \rangle ^{\frac{1}{2}} \) of thermal vibration of atoms in cubic crystals can be calculated if the Debye temperature \( \theta \) is known. The relation\(^1\) used is based on the Debye-Waller theory of temperature factor of X-ray scattering:

\[
\dot{a}^2 = \frac{436 \cdot 4T}{g^2} \left\{ \phi(x) + \frac{x}{4} \right\}
\]

where \( A \) is the atomic weight, \( T \) the absolute temperature, \( \phi(x) \) the Debye function and \( x = \theta / T \).

In a multi-atom crystal (compound), the left-hand side of equation (1) is usually replaced by \( A_1 u_1^2 + A_2 u_2^2 + \ldots + A_n u_n^2 \) where \( A_i \)'s and \( u_i \)'s are the atomic weights and the displacements of the constituent atoms respectively. Equation (1) can, however, be applied to cubic compounds with the assumptions that all the atoms vibrate with the same amplitude and the solid is composed of only one kind of atoms of atomic weight \( A \) given by

\[
A = (A_1 + A_2 + \ldots + A_n) / n
\]

The errors introduced in this way are probably less than those due to the uncertainty in the value of \( \theta \).

Between the purely ionic and covalent crystals there is a continuous range of crystals. It is often of importance to estimate in such cases the extent to which a given bond is ionic or covalent, but this may be difficult to do with any confidence. Nedyukha and Chernyi\(^2\) have pointed out that the amplitude of atomic vibration is a measure of the strength of interatomic bonding in solids. Since a covalent bond is stronger than an ionic bond, the amplitude of atomic vibration at a given temperature in the former case should be smaller than in the latter. Based on this argument, Sirdeshmukh and Rao\(^3\) have concluded by comparing the mean amplitude of TiO\(_2\) (0·104 \(\AA\)), MgF\(_2\) (0·139 \(\AA\)) and MnF\(_2\) (0·180 \(\AA\)) that the bonding in TiO\(_2\) may be covalent. This kind of reasoning in those solids where both ionic and covalent bonding exist may lead to, in certain cases, an erroneous result. The variation in amplitude of atomic vibration in the above three compounds is not very significant. This variation by a factor of two is also observed in purely covalent crystals, viz., diamond, silicon and germanium as shown in Table I; the same

\[
\text{Table I}
\]

<table>
<thead>
<tr>
<th>Covalent crystal</th>
<th>Ionic crystal</th>
<th>( \langle \dot{a}^2 \rangle ^{\frac{1}{2}} ) (\AA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond</td>
<td>Na(_2)Br</td>
<td>0·056</td>
</tr>
<tr>
<td>Si</td>
<td>NaF</td>
<td>0·0112</td>
</tr>
<tr>
<td>Ce</td>
<td>RbI</td>
<td>0·148</td>
</tr>
</tbody>
</table>

\( ^1 \) The value given here is different from that in the original paper. It appears that the term \( x/4 \) in equation (1) has not been taken into account.

is true in the case of purely ionic crystals. Under these conditions it is difficult to say with certainty about the nature of bonding simply by comparing the variations in \( \langle \dot{a}^2 \rangle ^{\frac{1}{2}} \). It is, however, to be noted (Table I) that the average amplitude of vibration for covalent crystals is of the order of 0·1 \(\AA\) while this in ionic crystals is about 0·2 \(\AA\). Hence the Debye-Waller factor for a multi-atom crystal cannot be used to decide whether the bonding is ionic or covalent.

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OXIDATIVE HYDROLYSIS OF SOME KETOXIMES BY THALLIC IONS

The formation of oximes and semicarbazones serves as a method for isolating and purifying carbonyl compounds. Various methods such as direct acid hydrolysis\(^1\), acid-catalyzed exchange with pyruvic acid\(^2\), etc., are available for generating the original aldehydes and ketones; some of these methods are drastic and besides the main oxidative hydrolysis, cause also the hydrolysis of sensitive protecting groups like acetoxyl groups. Recently, studies on the oxidative hydrolysis of oximes and semicarbazones by metal ions Ceriac\(^3\) and Thalliac\(^4\) were reported. The advantage of metal ions is that the yield of ketones is \( \geq 70\% \) and also the sensitive groups are not affected. The present investigation deals with the kinetic aspects of the oxidative cleavage of some ketoximes by Thallium(III) acetate.
Thallic acetate was prepared from Thallic oxide. Oximes of acetophenone, benzophenone, cyclopentanone and cyclohexanone were prepared by the standard methods. The compounds are repeatedly recrystallised to constant melting point. The melting points of acetophenone oxime, benzophenone oxime, cyclopentanone oxime and cyclohexanone oxime are 60°C (lit5, m.p. 60°C), 143°C (lit6, m.p. 144°C), 56.5°C (lit7, m.p. 56.5°C) and 89-90°C (lit8, m.p. 89-90°C) respectively. All the oximes are homogeneous in TLC. The kinetics was followed by estimating the rate of disappearance of Tl(III) by iodometry.

**Oxidation by Tl(III).**—The reaction, Tl-Oxime, in 50% (v/v) aqueous acetic acid [Tl\(^{3+}\)] = 1.25 × 10\(^{-3}\) M; [Oxime] = 8.0 × 10\(^{-3}\) to 2.0 × 10\(^{-2}\) M; [H\(^+\)] = \(\mu = 1\) M proceeds smoothly at measurable rates in the temperature range 20-45°C and was followed by estimating Tl(III) at definite intervals of time (> 10 minutes) except in the case of cyclohexanone oxime for which time interval was shorter (ca. 2 minutes). The overall order of the reaction was found to be two, the individual order with respect to [Oxime] and [Tl(III)] being one each. It was found that an increase in [H\(^+\)] at constant ionic strength of 2 M (NaHSO\(_4\)), decreases the rate. This may be attributed to the decrease in the active oxidant, [Tl(OAc)\(_2\)]\(^{3+}\), due to the following equilibrium,

\[
\text{Tl(OAc)}_2^{3+} + \text{H}^+ \rightleftharpoons \text{Tl(OAc)}_2^{2+} + \text{AcOH}
\]

The second order rate constants were obtained from plots of \(k_{\text{obs}}\) vs [Oxime] (Table I). From a plot of \(\log k_2\) vs 1/T, the Arrhenius energy of activation and the other thermodynamic parameters were evaluated (Table II).

The reaction, Tl-Oxime, being an ion-dipole reaction [Tl(III)—ion; Oxime—dipole] there will be electrostatic contribution involving ion-dipole interactions to the activation energy in addition to non-electrostatic contribution. Consequently \(\Delta S^\ddagger\) and \(A\) values are higher than the theoretical value expected for a second-order reaction. Such high values are also obtained for the oxidation of organic substrates by metal ions 10.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>(k_2 \times 10^3)</th>
<th>(\text{M}^{-2} \text{Sec}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetophenone oxime</td>
<td>6.43</td>
<td>15.06</td>
</tr>
<tr>
<td>Benzophenone oxime</td>
<td>.</td>
<td>.</td>
</tr>
<tr>
<td>Cyclopentanone oxime</td>
<td>5.36</td>
<td>12.50</td>
</tr>
<tr>
<td>Cyclohexanone oxime</td>
<td>176</td>
<td>250</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Substrate</th>
<th>E (kcal/mole)</th>
<th>A (M(^{-1}) Sec(^{-1}))</th>
<th>S (e.u./mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetophenone oxime</td>
<td>33.1</td>
<td>(1.21 \times 10^{22})</td>
<td>42.4</td>
</tr>
<tr>
<td>Benzophenone oxime</td>
<td>30.3</td>
<td>(2.29 \times 10^{19})</td>
<td>31.4</td>
</tr>
<tr>
<td>Cyclopentanone oxime</td>
<td>35.1</td>
<td>(2.69 \times 10^{23})</td>
<td>48.6</td>
</tr>
<tr>
<td>Cyclohexanone oxime</td>
<td>13.2</td>
<td>(8.42 \times 10^{8})</td>
<td>-16.9</td>
</tr>
</tbody>
</table>

X-RAY STUDIES IN THE SYSTEM 
\textbf{BaTiO}_3-\textbf{MoO}_3

The effect of various additives on the structural and electrical properties of \textbf{BaTiO}_3 has been reported\textsuperscript{4-5}. These additions yield compositions with potential industrial applications. This note summarises the effect of \textbf{MoO}_3 addition on the structural properties of \textbf{BaTiO}_3.

The method of preparation of the compounds is described\textsuperscript{4-5} elsewhere. The only difference is in the heat treatment. In the present case preiring was done at 500–600°C for 6 hr to avoid the loss of \textbf{MoO}_3. The losses after firing at 1300°C were 0.5% on a 10 g batch and hence no chemical analysis of the samples was necessary. Room temperature (25°C) X-ray diffraction powder photographs taken on a 14 cm diameter Debye-Scherrer camera with MoKα radiation filtered through Zr foil showed the existence of three phases: (1) \textbf{BaTiO}_3 phase at all compositions, (2) \textbf{TiO}_2 (rutil) phase beyond 3 mole% \textbf{MoO}_3 and (3) \textbf{BaMoO}_4 phase present even at as low as 0.2 mole% addition of \textbf{MoO}_3.

The variation of cell parameters of \textbf{BaTiO}_3 with \textbf{MoO}_3 addition shows (Table 1) a contraction in (c/a) increases with increasing \textbf{MoO}_3 incorporation till 2 mole% beyond which it drops to a constant value of 0.993, corresponding to the value obtained at about 1 mole% \textbf{MoO}_3 incorporation. The rate of increase of tetragonality (c/a) is 0.0038 per mole% \textbf{MoO}_3 for the first mole% addition, decreasing to 0.0020 for the second mole% \textbf{MoO}_3 incorporation. These results can be understood by considering that the primary function of the \textbf{MoO}_3 incorporation in the \textbf{BaTiO}_3 lattice is to introduce \textbf{BaO} defects through the formation of \textbf{BaMoO}_4. For larger concentrations of \textbf{MoO}_3, the perovskite (\textbf{BaTiO}_3) lattice no longer tolerates additional vacancies and a third phase (rutile) begins to crystallise beyond 2 mole% \textbf{MoO}_3. The presence of excess of \textbf{TiO}_2 in specimens containing \textbf{MoO}_3 ≥ 3 mole% seems to be the determining factor for the observation of a decrease in c/a ratio beyond 2 mole% \textbf{MoO}_3 incorporation, the reaction taking place for x ≤ 2 mole% being

\[
\text{BaTiO}_3 + x\text{MoO}_3 \rightarrow \text{Ba}_{1-x}\text{TiO}_2 + x\text{BaMoO}_4.
\]

The electrical properties are being reported elsewhere\textsuperscript{6}.


\begin{table}[h]
\centering
\caption{Lattice parameters and \(c/a\) ratio for the \textbf{BaTiO}_3-\textbf{MoO}_3 system}
\begin{tabular}{|c|c|c|}
\hline
Mole\% \textbf{MoO}_3 & \textbf{Cell parameters} & \(c/a\) \\
 & \(a\) & \(c\) & \\
\hline
0.00 & 4.03 & 3.993 & 0.989 \\
0.25 & 4.03 & 3.995 & 0.991 \\
0.50 & 4.03 & 3.998 & 0.992 \\
1.00 & 4.028 & 4.00 & 0.993 \\
1.50 & 4.026 & 4.002 & 0.994 \\
2.00 & 4.024 & 4.002 & 0.995 \\
2.50 & 4.029 & 4.00 & 0.993 \\
3.00 & 4.029 & 3.999 & 0.9928 \\
3.50 & 4.029 & 3.999 & 0.9928 \\
\hline
\end{tabular}
\end{table}

the \textbf{a} direction and an expansion in the \textbf{c} direction of the \textbf{BaTiO}_3 unit cell. The tetragonal strain

\textbf{OXIDATION OF THIOGLYCOLIC ACID USING DICHLORAMINE-T IN GLACIAL ACETIC ACID MEDIUM}

The mechanism of oxidation of thiols has received considerable attention\textsuperscript{1}. The sulphhydryl group in the compounds is converted into the corresponding disulphide with mild oxidants, while with stronger oxidants or under favourable experimental conditions, oxidation could proceed further leading to a sulphonic acid.

Recently, Jacob and Nair\textsuperscript{2} have reported on the use of dichloramine-T (N,N'-dichloro-p toluene sulphonamide, hereafter abbreviated to DCT) as a new oxidimetric titrant in aqueous and partially aqueous media. It has been found that thiglycolic